

(12) UK Patent Application (11) GB 2 147 305 A

(43) Application published 9 May 1985

(21) Application No 8422440

(22) Date of filing 5 Sep 1984

(30) Priority data

(31) 58/162903

(32) 5 Sep 1983

(33) JP

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(51) INT CL⁴
C08G 81/00 77/54

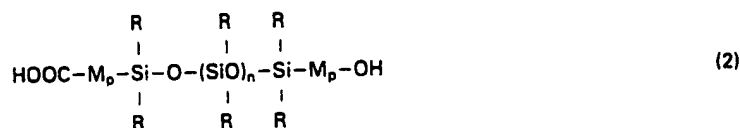
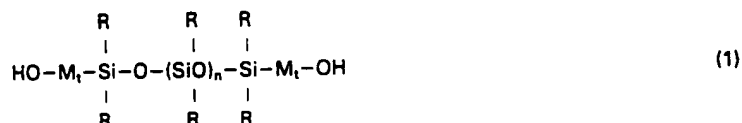
(52) Domestic classification
C3T 101 132 133 161 AM
U1S 1573 1575 1781 2030 3025 3026 3035 3042 C3T

(56) Documents cited
GB 1343783

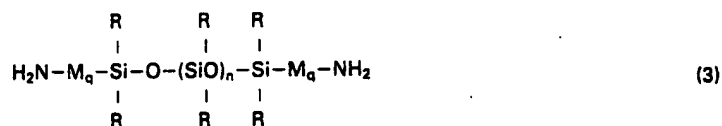
(58) Field of search
C3T

(54) Process for producing polyamide/polysiloxane block

(57) A carboxyl-terminated or amine terminated polyamide is coupled with one or more polysiloxanes of the formulae



and



by way of a compound having two isocyanate groups. (R is H, methyl or phenyl; M is alkylene, phenylene or oxyethylene; p, q, t are each 0-5; n is 0-50)

The resulting block copolymer may be used in the production of hoses, tubes, seals and caterpillar belts.

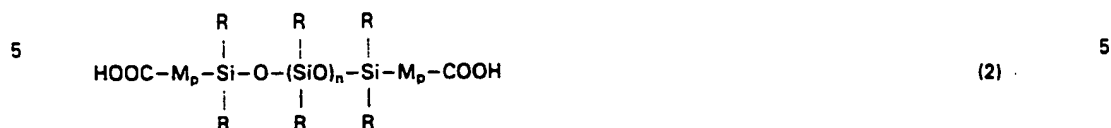
SPECIFICATION

Process for producing polyamide/polysiloxane block copolymer

- 5 This invention concerns a process for producing a novel polyamide/polysiloxane block copolymer. 5
 More specifically, it relates to a process for producing a novel polyamide/polysiloxane block copolymer obtained by coupling a polyamide polymer and a polysiloxane polymer by way of urethane bonds.
 Resins or resin mixtures containing polysiloxane polymer have been noted in recent years. As is well known, since polysiloxane polymers have excellent physico-chemical properties such as heat resistance and
 10 cold resistance, they are used practically as primary products such as rubbers (silicone rubber), oils and varnishes, as well as various secondary products prepared from them. Furthermore, studies have been made recently in a wide variety of fields for developing various functions of polysiloxane polymers while maintaining the foregoing physiochemical properties. For instance, a study has been made in the field of engineering plastics for preparing tubes or hoses with high impact resistance at low temperature by utilizing
 15 the low temperature elasticity of the polymers. Due to their biochemical stability, various products have already been put to practical use in the field of medicine, for example, as orthopaedic materials, reparatory material, for veins or the like, and base materials for ointments. Furthermore, polysiloxane polymers have now attracted attention due to their utility in the field of gas separation membranes, from the resource-saving and energy-saving point of views. The gas separations meant herein are the purification of
 20 helium, separation of rare gases, concentration of uranium, enrichment of oxygen, and separation and purification of recycle gases, for example, in the synthesis of methanol and acetic acid. Of these, oxygen enrichment membranes have already been put to practical use for the improvement of the fuel efficiency of boilers.
 Processes for producing resins or resin mixtures containing polysiloxane polymers include the following:
 25 (1) A method of direct mixing of a polysiloxane polymer with another resin has already been described, for instance, in Japanese Patent Laid-Open No. 93749/1983, *Plastics World*, p70, March, 1983 and the like.
 (2) A method of producing a block copolymer by chemically bonding a polysiloxane polymer with another polymer such as polyester, polyether, polyurethane or polycarbonate is described, for example, by W. L. Roff, *Ann. N.Y. Acad. Scie.*, 146, 119 (1967), W. J. Ward, *J. Mom. Sci.*, 1 and USP 3,781,378.
 30 (3) A method of graft polymerizing a polysiloxane onto an appropriate skeleton polymer is described, for example, in Japanese Patent Laid-Open No. 135007/1982, *Proceedings of High Molecule Society* 31, 461 (1982).
 (4) A process for synthesizing a high polymer through anionic polymerization of radicals containing polysiloxane on the side chain as a substituent radical is described, for example, in Japanese Patent
 35 Publication No. 21021 1977.
 Among the various production processes described above, the process suitable for adjusting the mechanical, electronic and physical properties of the resin dependant on its use is considered to be the process of preparing a block copolymer by chemically bonding a polysiloxane copolymer with another polymer as described in (2) above in view of the easy molecular design.
 40 As the result of earnest study, the present inventors have discovered a process for producing a novel polyamide/polysiloxane block copolymer possessing such excellent properties of polyamide resins as mechanical strength, abrasion resistance, gasoline-resistance and lubricant-resistance whilst further introducing heat resistance, water absorption resistance and chemical resistance, by coupling a polyamide polymer and a polysiloxane polymer through adequate urethane bonds.
 45 Specifically, this invention provides a process for producing a polyamide/polysiloxane block copolymer, wherein a dicarboxylic polyamide having a carboxyl group in both terminal positions or a diamine polyamide having an amide group in both terminal positions and having a number average molecular weight of from 500 - 10,000 prepared either by polycondensation of a lactam or α,ω -amino acid having 2 - 15 carbon atoms in the hydrocarbon chain or by polycondensation of a dicarboxylic acid with a diamine having
 50 2 - 15 carbon atoms in the hydrocarbon chain and having either carboxylic groups or amino groups at both of the terminal ends is coupled by way of a compound having two isocyanate groups with one or more polysiloxanes selected from polysiloxanes having a number average molecular weight of from 200 - 20,000 and having hydroxyl groups, amino groups or carboxylic groups on both terminal ends represented by the following formulae (1), (2) or (3):



(where M represents an alkylene group, phenylene group or oxyethylene group, R represents H, CH₃ or phenyl group and n is between 0 - 50 and t is between 0 - 5),



10 (where M and R have the same meanings as in the formula (1), and n is between 0 - 50, p is between 0 - 5)



(where M and R have the same meanings as in the formula (1), and n is between 0 - 50, q is between 0 - 5).

The dicarboxylic acid polyamide having carboxyl groups at both of the terminal ends of the diamine polyamide having amino groups at both of the terminal ends usable in this invention can be obtained by known processes. Thus, the polycondensation reaction referred to above may be carried out in the presence of a dicarboxylic acid or an organic diamine (these functional groups preferably situated at the terminal end of the hydrocarbon chain). These dicarboxylic acids or diamines are bonded in the course of the polycondensation reaction forming a high molecular polyamide chain. Alternatively, the α,ω -dicarboxylic acid polyamide or α,ω -diamine polyamide can be obtained by adding dicarboxylic acid groups or diamine groups to the terminal ends of the chain. Furthermore, the dicarboxylic acid or diamine may serve as the chain length controller. Thus, the α,ω -dicarboxylic acid or α,ω -diamine may be used in amounts in excess of that required to give a dicarboxylic polyamide or diamine polyamide of a predetermined molecular weight and by properly selecting the degree of the excess, the length of the polymer chain, that is, the average molecular weight of the polyamide, can be controlled.

The specific method of this invention for preparing a polyamide/polysiloxane block copolymer may be carried out by first reacting a polyamide with a compound having two isocyanate groups and then reacting a polysiloxane therewith, or by first reacting a polysiloxane with a compound having two isocyanate groups and then reacting a polyamide therewith. Similar polyamide/polysiloxane block copolymers can be obtained by either sequence.

The polyamide usable in this invention may be prepared starting from lactams or α,ω -amino acids having 2 - 15 carbon atoms in the hydrocarbon chains, for instance, caprolactam, enantholactam, undecanolactam, dodecanolactam, 11-amino-undecanoic acid, 12-aminododecanoic acid.

The polyamide usable in this invention may also be condensation products of a dicarboxylic acid and a diamine, for example, condensates of hexamethylene diamine and adipic acid, azelaic acid, sebacic acid or 1,12-dodecanoic diacid, as well as nylon 6-6, 6-9, 6-10, 6-12 and 9-6 which are the condensates of nonamethylene diamine and adipic acid.

The dicarboxylic acid or the organic diamine used as the chain length controller in the synthesis of the polyamide enables a polyamide having either carboxyl groups or amino groups at both of the terminal ends to be obtained. The preferred dicarboxylic acids include aliphatic dicarboxylic acids with 2 - 15 carbon atoms and the preferred diamines include aliphatic diamines with 5 - 14 carbon atoms.

Cycloaliphatic or aromatic dicarboxylic acids or diamines can also be used. These dicarboxylic acids or diamines are used in amounts in excess of the amount required for obtaining a polyamide having a desired average molecular weight in accordance with the known method of calculation employed at present in the field of polycondensation.

The average molecular weight of the dicarboxylic acid polyamide or diamine polyamide usable in this invention is between 500 - 10,000 and, preferably, 800 - 5,000.

The isocyanate compound having isocyanate groups at the terminal ends of the chain usable in this invention may be of straight chained or branched structure and cycloaliphatic or aromatic compounds can be used in addition to the aliphatic compounds. They include, for instance, tetramethylene diisocyanate, hexamethylene diisocyanate, octamethylene diisocyanate, nonamethylene diisocyanate, dodecamethylene diisocyanate. The average molecular weight of the polymethylene diisocyanate is between 50 - 8,000 and, preferably, 100 - 5,000. The diisocyanate compound as described above can be used by an amount from equimolar to two molar amount based on the amount of the dicarboxylic polyamide or diamine polyamide. The reaction should occur at such a low temperature as not to cause side reactions since the isocyanate group is active to the amino group (the reactivity is lowered from the primary amino group to the secondary amino group).

As catalysts for use in the reaction between the polyamide and the diisocyanate compound, tertiary amines or heavy metal derivatives (such as those derived for example, from diazabicyclo octane or diazabicyclo undecene) are suitable and also dibutyltin dilaurate, zinc dilaurate, lead dilaurate and the like.

However, in the reaction of the diamine polyamide and the diisocyanate compound, the reaction can proceed at a sufficient rate in the absence of the catalyst, although the use of the catalyst causes no problems. Specifically, the reaction between the dicarboxylic polyamide or diamine polyamide and the diisocyanate compound, the catalyst as described above can be used solely or together with an alkali metal or alkaline earth metal alcoholate in an amount between 0.01 - 2% by weight, and preferably, 0.03 - 1% by weight based on the total weight of the reaction mixture.

The isocyanate-terminated polyamide urethane synthesized as described above is further reacted with a polysiloxane having the various functional groups as described previously in the formulae (1), (2) (3) as the soft segment in the presence or absence of the catalyst as described above. The average molecular weight of the polysiloxane usable herein is between 200 - 20,000 and, preferably, 300 - 18,000. The appropriate ratio of the polysiloxane employed is between 0.95 - 1.05 mol based on the total amount of the diisocyanate polyamide urethane.

As the reaction solvent, polar solvents, as well as halogenated aliphatic or aromatic solvents are used and they can include, for example, N,N-dimethylamide, N,N-dimethylformamide, hexamethylphosphortriamide, m-cresol, o-dichlorobenzene, chlorobenzene and phenol.

The amount of the solvent employed can be varied in a wide range and it is generally between 50 - 95% and, preferably, between 60 - 80% by weight based on the total amount of the reaction product.

The polycondensation for obtaining the block copolymer can be carried out by merely heating the reaction mixture to a temperature range between 110 - 180°C, and, preferably, between 120 - 160°C. When adding the reaction ingredients, each of the reaction ingredients is added dropwise and the resultant copolymer is separated, after the completion of the reaction, from the reaction mixture and purified for recovery by known methods.

The process according to this invention can advantageously be carried out in two steps. Thus, for example, in the first step, either one of the polyamides, i.e. that with carboxyl groups at both terminals or that with amine groups at both terminals, is reacted with some or all of the diisocyanate compound in the solvent and, in the second step, one of the polysiloxanes selected from those having diols, dicarboxylic acids and diamines at both terminal ends is introduced into the same solvent to produce a polyamide/polysiloxane block copolymer.

The block copolymer according to this invention, has excellent physical properties, and is suitable for use in the production of hoses, tubes, sealing materials such as seals and packings or belts such as caterpillar belts.

This invention will be further illustrated with reference to the following examples, but it should be noted that this invention is in no way limited thereto.

35 Example 1

To a four-necked flask equipped with a cooling tube, a dropping funnel, a stirrer and a nitrogen introduction pipe, were charged 50 ml of chlorobenzene and 50 ml of phenol. 25g (10.6 mmol) lauryllactam oligomer having amine groups at both terminal ends (number average molecular weight $\overline{M}_n = 2300$) were added while nitrogen gas was bubbled through the mixture, warmed to 110°C and then gradually cooled nearly to room temperature. 5.5g (21.7 mmol) of dodecamethylene diisocyanate were then gradually added over a period of about 5 minutes using a dropping funnel, whilst the mixture was vigorously stirred. Stirring was continued for a further period of about 30 minutes. Then, 18.5g (10.6 mmol) of polydimethylsiloxane terminated with hydroxy groups at both ends mixed with 4 W% solution of DBU (diazabicyclo undecene) in 0.1 ml N,N-dimethylacetamide and 20 ml of chlorobenzene were added dropwise using a dropping funnel whilst stirring at room temperature for about 30 minutes. After the completion of the dropwise addition the mixture was refluxed at 130°C for one hour. The reaction product was precipitated in methanol, finely pulverized therein by a pulverizer and then dried in vacuo (0.1 mmHg) at 80°C for 3 hours.

The solvent used herein was prepared through fractionation, followed by sufficient drying by the addition of zeolite A-3 8 - 12 mesh (manufactured by Wako Junyaku).

The plate-like body of about 2 mm thickness obtained through compression moulding of the thus obtained powdery polymer specimen showed the following physical properties.

Glass transition point (T_g (°C)) 163.

Recrystallization point (T_c (°C)) 98 (Measurement was carried out by using a differential thermal analyzer).

Tensile strength at 20°C : 438 kg/cm² (according to JIS K-7113)

55 Elongation at break at 20°C : 183 % (according to JIS K-7113).

Example 2

Using the same apparatus as in Example 1, 100 ml of chlorobenzene and 50 ml of phenol were charged in a reaction vessel and 25g (10.6 mmol) of lauryllactam oligomer having amine groups at both terminal ends ($\overline{M}_n = 2300$) were added while nitrogen gas was bubbled through the mixture, the mixture was then warmed to 130°C and then gradually cooled nearly to room temperature. 5.48g (21.7 mmol) of dodecamethylene diisocyanate were gradually added over a period of 5 minutes using a dropping funnel while vigorously stirring the mixture inside the reaction vessel. The stirring was continued for a further period of about 30 minutes. Then, 26.0g (10.9 mmol) of polydimethyl siloxane having carbinol groups at both terminal ends ($\overline{M}_n = 2400$) diluted with 50 ml of chlorobenzene were gradually added dropwise for about one hour, in the

absence of catalyst. After the completion of the dropwise addition, the mixture was refluxed at 130°C for one hour. The reaction product was precipitated in methanol, pulverized therein and then dried in a vacuum drier (0.1 mmHg) at 80°C for about 3 hours.

The plate-like body of about 2 mm thickness obtained by compression moulding of the thus obtained powderous specimen showed the following physical properties.

Glass transition point (T_g (°C)) : 165

Recrystallization point (T_c (°C)) : 105

Tensile strength at 20°C : 522 kg/cm²

Elongation at break at 20°C : 300 %.

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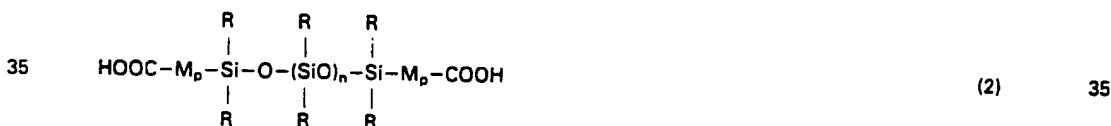
CLAIMS

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1. A process for producing a polyamide/polysiloxane block copolymer, wherein a dicarboxylic polyamide having a carboxyl group in both terminal positions or a diamine polyamide having an amine group in both terminal positions and having a number average molecular weight of from 500 - 10,000 prepared either by polycondensation of a lactam or, -amino acid having 2 - 15 carbon atoms in the hydrocarbon chain or by polycondensation of a dicarboxylic acid with a diamine having 2 - 15 carbon atoms in the hydrocarbon chain and having either carboxylic groups or amino groups at both of the terminal ends is coupled by way of a compound having two isocyanate groups with one or more polysiloxanes selected from polysiloxanes having a number average molecular weight of from 200 - 20,000 and having hydroxyl groups, amino groups or carboxylic groups on both terminal ends represented by the following formulae (1), (2) or (3):



(where M represents an alkylene group, phenylene group or oxyethylene group, R represents H, CH₃ or phenyl group and n is between 0 - 50 and t is between 0 - 5),



(wherein M and R have the same meanings as in the formula (1), and n is between 0 - 50, p is between 0 - 5),



(where M and R have the same meanings as in the formula (1), and n is between 0 - 50, q is between 0 - 5).

2. A process as claimed in claim 1, in which the mole ratio of isocyanate to polyamide is from 1 to 2.
3. A process as claimed in claim 1 or 2, in which the polyamine is first reacted with some or all of the isocyanate to form diisocyanate polyamide urethane and the polysiloxane then reacted with the resulting mixture.
4. A process as claimed in claim 3, in which the ratio of polysiloxane to diisocyanate polyamide urethane is from 0.95 to 1.05.
5. A process as claimed in any of claims 1 to 4, in which the reaction between the polyamide and the isocyanate is carried out in the presence of a catalyst.
6. A process as claimed in any of claims 1 to 5, in which a solvent is present in the reaction mixture in an amount of from 50 to 95% of the reaction mixture.
7. A process as claimed in claim 1, substantially as hereinbefore described in any one of the Examples.